Toughening of Wood-plastic Composites Based on Silane/Peroxide Macro Crosslink Poly(propylene) Systems

Utai Meekum,* and Anuchit Khongrit

The toughening of wood-plastic composites (WPC) based on silane/ peroxide macro crosslink poly(propylene) (PP) systems was studied. A 2^3 experimental design was adopted to initially optimize three parameters: silane, wood flour, and talc contents of the WPC formulation. The WPCs were manufactured on a co-rotation twin screw extruder. Test specimens were prepared *via* injection molding. The WPC compounding formula with 8 phr of silane, 35 phr of wood flour, and 20 phr of talc was used to study the effect of ultra-high molecular weight polyethylene (UHMWPE) as a toughener. The impact strength was improved up to a 10-phr UHMWPE loading. The flexural properties and heat distortion temperature (HDT) slightly decreased. When exceeding 10 phr of UHMWPE, the unmelted UHMWPE agglomerated and the mechanical properties were inferior. The fiber/matrix interfacial adhesion was enhanced by the sauna treatment. A marginal increase in the fracture toughness was observed. The impact strengths increased with the addition of ethylene propylene diene terpolymer (EPDM) as a rubber toughener. However, high EPDM contents caused a decrease in the HDT. The sauna incubation of the EPDM-toughened WPC enhanced the impact strengths. The EPDM effectiveness was determined by the better PP matrix toughness and UHMWPE/PP interfacial adhesion.

Keywords: Wood-plastic composite; Silane/peroxide crosslink; PP and UHMWPE/EPDM toughener

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INTRODUCTION

Typically, wood-plastic composites (WPCs) are a material manufactured from thermoplastics that are reinforced with natural fibers. They are used as a substitute or alternative for natural wood, which is widely prohibited or legally controlled by many countries. Building and decorative materials, such as outdoor decks, floors, windows, and doors, are their main applications. Polyolefins, such as poly(vinyl chloride) (PVC), poly(propylene) (PP), and poly(ethylene) (PE), are currently used as commercial matrices. There are advantages and disadvantages to these matrices. For example, PP-WPCs are easy to process, but they have a low ultraviolet radiation resistance. The PE-WPC offers decent melt processing, but it has a low service temperature. The PVC-WPC has an outstanding resistance to environmental deterioration, but is harmful during melt extrusion. There have been many studies into how to bypass these weaknesses.

There are numerous reports on wood flour/PP composites made with various wood flour particle sizes. It has been found that the mechanical properties of composites depend on the fiber aspect ratio (Stark and Rowlands 2003). Additionally, the mechanical properties of WPCs are affected by the type of fibers used (Zaini *et al*. 1996; Febrianto *et al*. 2006; Khan *et al*. 2009). Improving their long-term properties has been of interest and

explored by many researchers. Grafting, crosslinking and matrix blending, fiber modification, and adding high performance fillers are among the typical methods studied in previous literature (Bengtsson and Oksman 2006; Lei *et al*. 2007; Clemons 2010). Silane grafting followed by a water crosslink reaction of the polymer matrix to form a loosely macro crosslink chain, especially with PP and PE, has received much attention in industrial applications and fundamental research (Zhou *et al*. 2009). The crosslink reaction mechanism is illustrated in Fig. 1. The macro crosslink provides obvious advantages, such as easy processing, low capital investment, and favorable properties in the processed materials (Sirisinha and Kawko 2005). Vinyl silane is chemically grafted onto the polymer chain by free radicals using peroxide as an initiator. Then, it is hydrolyzed and condensed to create –Si–O–Si– bonds between the chains and/or bonding between the wood and polymer. The macro crosslink, *via* silane bridges, results in outstanding performance properties.

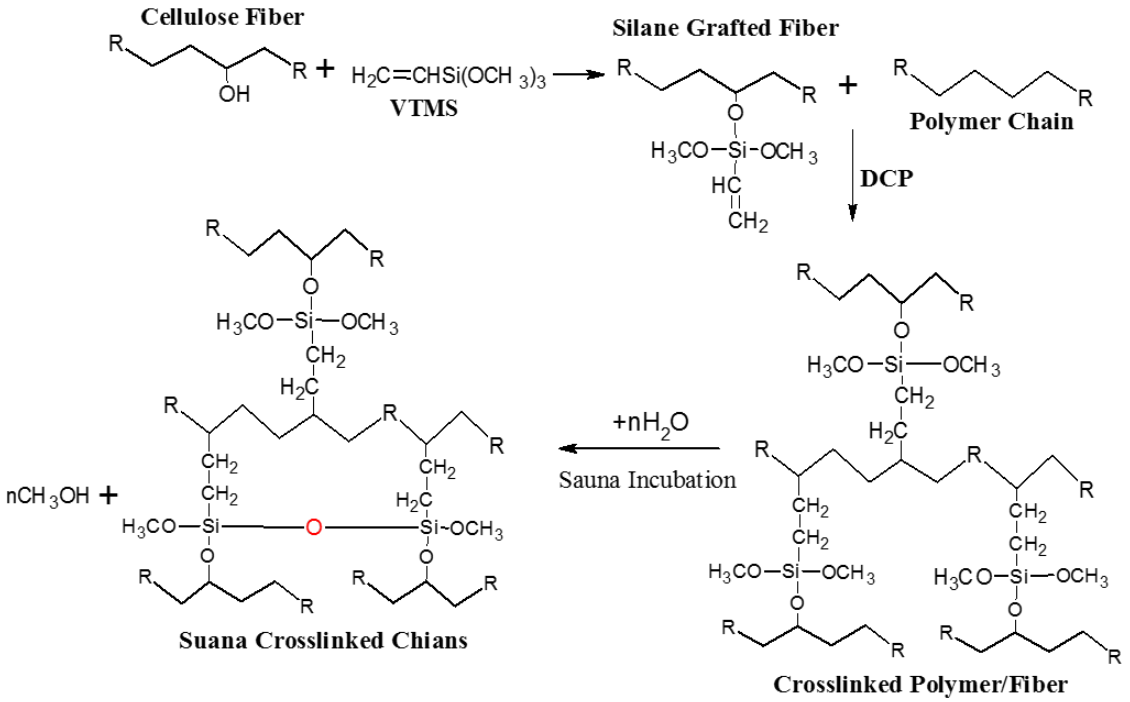

Fig. 1. Schematic illustration of the fiber/polymer crosslinking *via* peroxide/silane condensation

The flammability, fracture toughness, and impact resistance of WPCs are commonly among the most important properties for different applications. Typically, WPCs are subjected to bending loads during application. To achieve the highest load bearings possible, various modifications have been used, such as toughening of the matrix by blending with a stiffer polymer, rubber toughening, hybridization of the natural fiber with engineering reinforcement, and/or filling with inorganic particles (Hristov *et al.* 2004). Polymer blends have been extensively studied and highly successful in improving the properties of WPCs. The benefits include improvement of the impact strength, tensile strength, environmental stress cracking, low temperature impact properties, and more. Studies into PP/PE blends are the most common and have gained much attention (Wang *et al.* 1995). Investigation of WPCs produced from ternary blends from recycled PP/low-density PE/high-density PE (HDPE) containing date palm fibers and flame retardants showed that the retardants reduced the mechanical properties and the palm fibers

strengthened the whole composite. This helped to simultaneously achieve flame retardancy and better mechanical properties (Zadeh *et al*. 2017). Microfibrillar blends of WPCs are produced by the extrusion of poly(ethylene terephthalate) (PET)/HDPE blends reinforced with 25% *in situ* formed PET microfibers, 2% maleated polyethylene (E-GMA), and 40% wood flour. The mechanical properties were obviously increased. A remarkable enhancement by the *in situ* formed recycled PET microfibers was observed by Lei and Wu (2010). Rubber toughening methods have also gained a lot of attention. The fracture resistance of WPCs manufactured from PP toughened with ethylene propylene diene terpolymer (EPDM) elastomers has also been studied. Slight increases in the impact resistance of the wood were observed. The added elastomer was drastically separated into two components. Therefore, the fracture toughness remained small in the phase separated structure (Sudár *et al*. 2016). Massive cracking induced by adding rubber particles has been clearly observed in WPCs made from a high impact polystyrene matrix. The effectiveness of the rubber as a toughener was less pronounced (Pearson *et al*. 2000).

Treatment or modification of the fiber is one of the main ways to enhance the properties of WPCs. Treating beech wood fibers with emulsified methylene diphenyl diisocyanate resin before compounding with HDPE has been explored. Reducing the water absorption and improving the flexural strength were the main advantages for the resultant WPC (Schirp *et al*. 2014). Inorganic fillers, especially silica-based minerals, are also used as a main filler to improve properties. Silicate-based minerals treated with an amino type silane are used as the filler in WPCs made from maple wood flour/HDPE. It has been reported that adding 1% silane-modified minerals decreases the rigidity of the wood, but increases the ductility by up to 25%. Alternatively, mineral fillers modified with vinyl silane were more effective at improving both the tensile and flexural strengths and less effective at improving the rheological behaviors (Koohestani *et al*. 2017).

In this study, WPCs made with silane/peroxide crosslink PP matrix and wood flour reinforcement were investigated. Improving the service temperature and mechanical properties, especially the toughness, was the main aim of this research. The main ingredients of the WPCs were PP, wood flour, talc filler, and vinyl type silane. A design of experiment (DOE) was adopted to determine the initial formulation. Ultra high molecular weight polyethylene (UHMWPE) and EPDM rubber were employed for toughening purposes.

EXPERIMENTAL

Materials

Commercial injection molding grade PP homopolymer (PP 700J) was employed as a matrix. It was kindly supplied by SCG Chemical Co., Ltd. (Bangkok, Thailand). Vinyltrimethoxy silane (VTMS, Silquest®A-171) was used as a crosslink agent and was purchased from Optimal Tech Co., Ltd. (Bangkok, Thailand). Dicumyl peroxide (DCP) was employed as a free radical initiator. It was supplied by Thai Poly Chemical Ltd. (Sumutsakorn, Thailand). Talc (Jetfine® 8CF) with an average particle size of 1.1 µm was purchased from Imerys Talc Luzenac France (Luzenac, France). The combined powder of tris(2,4-di-tert-butylphenyl) phosphate (Irgafos 168) and octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate (Inganox 1076) was mixed at a ratio of 1:1 by weight and was employed as a heat/processing stabilizer. These chemicals were supplied by Ciba Specialty Chemicals Corp. (Tarrytown, USA). Additionally, the UHMWPE (UH900) was bought

from Asahi Chemical Industry Co., Ltd. (Osaka, Japan). Ethylene propylene diene terpolymer (Royalene 301T) was also used as a rubber toughener and was from Lion Copolymer Geismar, LLC (Geismar, LA, USA). All of the ingredients employed were used as received to prepare the WPC samples.

Wood flour from a local timber mill (Cherdchia Ltd., Nakron Ratchasima, Thailand) was ground into a fine powder with a hammer mill machine (Retsch SR 200 Grauβ, Haan, Germany). The size of the fiber was selected by the machine sieve mesh size. For example, fiber obtained using a 1-mm sieve was assigned a particle size of less than 1 mm. The flour was vacuum-dried at 105 °C for at least 12 h. Then, it was treated with VTMS in a mixer chamber on high speed for 5 min. The silane-treated wood flour was subsequently stored overnight at room temperature to allow the completion of the wood/silane grafting reaction.

WPC manufacturing

The WPC manufacturing process by twin screw melt mixing is schematically shown in Fig. 2. The PP pellet was coated with DCP by adding the solid peroxide to the warmed polymer pellet in a tightly sealed bag and vigorously shaking the ingredients; thus the liquidized DCP was evenly coated onto the PP pellet. The talc, which was vacuum-dried at 110 °C for 3 h, and silane-treated wood flour were pre-blended with the DCP-coated PP. The solid mixture was then constantly fed into a co-rotation twin screw extruder (Brabender Model PL2100; Brabender®GmbH & Co. KG, Duisburg, Germany) using a single screw feeder. The segmented twin screws (25 mm in diameter and length/diameter = 20) were equipped with a section of three triple kneader disks. The barrel temperature profiles were electrically controlled at 180 °C, 185 °C, 185 °C, 190 °C, and 190 °C from the hopper to die zone. The extrudate strand was air-cooled and granulated. The wood composite pellet was dehumidified at 80 °C in a vacuum oven for 2 h before injection. The test specimens were manufactured by injection molding using a Tederic TRX60c injection molding machine (Tederic Machinery Co., Ltd., Zhejiang, China). The barrel temperatures were 170 °C, 170 °C, 175 °C, 190 °C, and 190 °C from the feed to nozzle. Four rectangular shaped-mold cavities with tab gates were employed. The mold temperature was set at 45 °C with a cooling time of 30 s.

When manufacturing the WPCs with UHMWPE and EPDM, the EPDM rubber and DCP were plasticized on a two-roll mill (Chaicharoen Karnchang, Bangkok, Thailand). Then, a pre-calculated amount of the UHMWPE powder, talc, and heat/processing stabilizer powder were added to the rubber. All of the ingredients were further incorporated by the folding/kneading actions of the mill until thorough dispersion was achieved. The rubber compound was finally kneaded into an approximately 3-mm-thin sheet and frozen in a deep freezer overnight. The frozen rubber sheet was immediately crushed into small pieces using a crushing machine (Philips HR 1791, Philips Indonesia Ltd., Jakarta, Indonesia). Finally, the rubber compound flakes were pre-blended with the PP pellet and VTMS-treated wood flour in a high-speed mixer chamber. Eventually, all ingredients were melt mixed in the twin screw extruder and injected into test specimens in the exact manner described earlier.

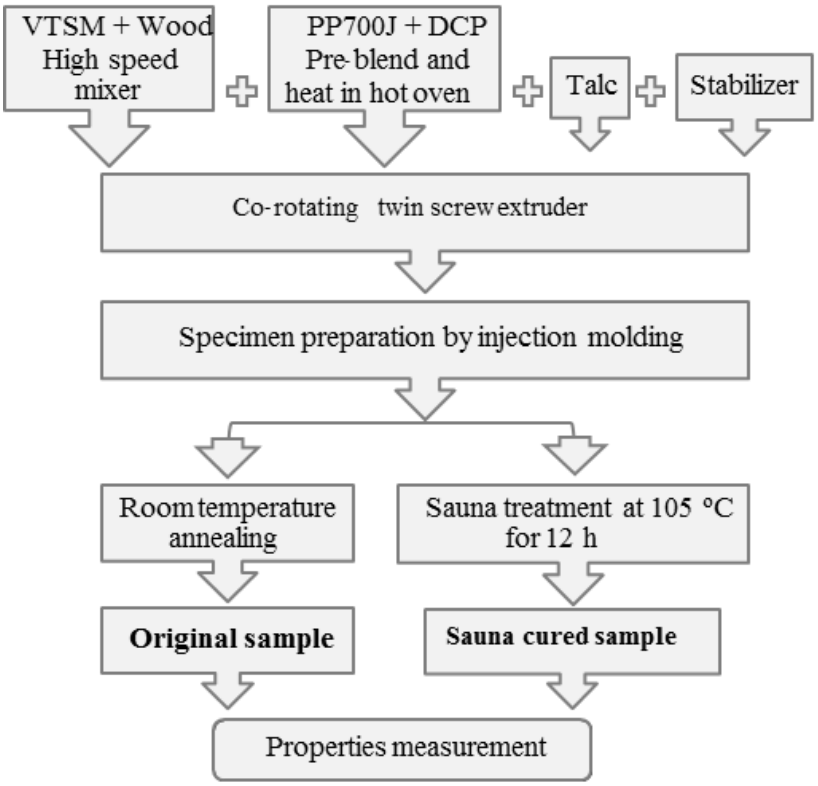

Fig. 2. Schematic diagram for the preparation of the PP-based WPC specimens

The injected PP-based WPC specimens were equally divided into two sets of samples. One was allowed to anneal at room temperature for at least a day before testing. It was named the "original" sample. The second set was placed in a moisture saturated oven at 105 °C for 12 h, which was called sauna incubation or sauna curing. Then, the samples were allowed to cool down in open air at room temperature for a day prior to testing and were referred to as "cured". The sauna incubation was performed to accelerate silane/water crosslinking *via* the condensation reaction (Zhou *et al*. 2009; Meekum and Kingchang 2017).

Methods

Determination of the rheological properties by means of the melt flow index (MFI) was performed in accordance with ASTM D1238-13 (2013) using a Kayeness melt flow indexer **(**Dynisco, Inc., Franklin, USA) at 170 °C and 2.16 kg. The three-point bending flexural test from ASTM D790-10 (2010) was performed on a 5-kN UTM testing machine (Instron Model 5565, Norwood, USA). The Izod mode impact strengths, both notched and unnotched, were measured in accordance with ASTM D256-10e1 (2010) using an impact testing machine with a 2.7-J impactor (Atlas Model BPI, Atlas Material Testing Technology LLC, Mount Prospect, IL, USA). The heat distortion temperature (HDT) was examined using an Atlas testing machine (HDV1, Atlas Material Testing Technology LLC, Mount Prospect, IL, USA), and ASTM D648-07 (2007) was followed with a 455-kPa standard load. The morphology of the notched impact specimens was investigated by means of scanning electron microscopy (SEM). The JSM 6400 SEM machine from JEOL Ltd. (Tokyo, Japan) was employed. The DOE analysis with the degree of confidence at

95% ($\alpha = 0.05$) was performed using Design Expert™ Version 8 software (Stat-Ease Inc., Minneapolis, USA).

RESULTS AND DISCUSSION

DOE: WPCs Based on Silane/Peroxide Macro Crosslink PP System

The 2^k factorial DOE, which had a $k = 3$, was selected to initially optimize and quantify the wood composite formulation. The chosen design parameters (k) were the contents of silane (A), wood flour (B), and talc (C). Obeying the rule of design, each parameter was divided into high (+) and low (-) levels. For statistical purposes and in order to have the randomize area, in high and low levels, they were also divided into two sub-levels, which are shown in Table 1. According to the 2^3 factorial DOE, eight absolute difference runs ($2^3 = 8$) were constructed as the design matrix, which are presented in Table 2. The DCP and heat/processing stabilizer were held constant in each formula at 0.3 phr and 2.0 phr, respectively.

Table 1. Design Parameters and Levels

Parameters	High Level (+)		Low Level (-)	
(**A**) Silane (phr)	10	8	-5	-3
(**B**) Wood flour (phr)	45	35	-25	-15
(**C**) Talc (phr)	40	30	-20	-10

Table 2. 2^3 Design Matrix

Run No.	PP (phr)	Silane (**A**) (phr)	Wood (**B**) (phr)	Talc (**C**) (phr)	DCP (phr)	Stabilizer (phr)
1	100	3 (-)	25 (-)	20 (-)	0.3	2
2	100	5 (-)	15 (-)	40 (+)	0.3	2
3	100	3 (-)	45 (+)	10 (-)	0.3	2
4	100	5 (-)	35 (+)	30 (+)	0.3	2
5	100	8 (+)	15 (-)	10 (-)	0.3	2
6	100	10 (+)	25 (-)	40 (+)	0.3	2
7	100	8 (+)	35 (+)	20 (-)	0.3	2
8	100	10 (+)	45 (+)	30 (+)	0.3	2

The WPC formulas from each experimental run were compounded in a randomized fashion, and the design responses obtained from both the original and cured injected WPC specimens are summarized in Table 3. The individual responses were used in the DOE statistical analyses with a 95% degree of confidence level ($\alpha = 0.05$) using the analysis software. Both an analysis of variance (ANOVA) and pareto charts were used to determine the significant effect of the design parameters, both individually and as interactions, and the responses. Then, the significant parameter(s) for each response was correlated into a linear regression equation, which is called optimization. Table 4 illustrates the optimal regression models between the design parameter(s) and given responses.

Table 3. Summary of the Responses for Each Experimental Run

Run No.	MFI (g/10 min)	Flexural Properties			
		Strength (MPa)		Modulus (GPa)	
		Original	Cured	Original	Cured
1 (-, -, -)	12.73	53.57 ± 0.71	53.57 ± 0.73	1.84 ± 0.16	1.96 ± 0.74
2 (-, -, +)	11.63	55.57 ± 0.63	54.17 ± 0.79	2.34 ± 0.07	2.41 ± 0.92
3 (-, +, -)	8.61	53.81 ± 0.83	53.75 ± 2.03	2.16 ± 0.06	2.18 ± 0.36
4 (-, +, +)	9.02	54.66 ± 1.19	55.69 ± 1.52	2.34 ± 0.05	2.35 ± 0.14
5 (+, -, -)	20.41	55.87 ± 0.72	57.67 ± 0.96	1.84 ± 0.02	1.88 ± 010
6 (+, -, +)	12.54	54.69 ± 1.91	54.12 ± 0.98	2.43 ± 0.10	2.58 ± 0.08
7 (+, +, -)	9.95	56.12 ± 1.21	57.44 ± 0.98	2.29 ± 0.10	2.23 ± 0.05
8 (+, +, +)	7.24	55.79 ± 1.33	56.04 ± 1.17	2.47 ± 0.13	2.57 ± 0.10

Run No.	Impact Strength (kJ/m^2)				HDT (°C)	
	Notched		Unnotched			
	Original	Cured	Original	Cured	Original	Cured
1 (-, -, -)	0.97 ± 0.14	1.43 ± 0.18	9.18 ± 0.25	8.94 ± 1.58	130.0 ± 2.0	136.7 ± 2.1
2 (-, -, +)	0.91 ± 0.10	1.35 ± 0.27	7.56 ± 1.39	7.70 ± 1.32	138.0 ± 0.0	138.7 ± 2.5
3 (-, +, -)	1.21 ± 0.26	1.32 ± 0.20	7.33 ± 1.27	8.69 ± 1.81	141.0 ± 1.7	141.0 ± 3.0
4 (-, +, +)	0.99 ± 0.19	1.48 ± 0.34	8.92 ± 1.16	6.28 ± 1.06	141.3 ± 1.2	143.3 ± 0.6
5 (+, -, -)	0.96 ± 0.11	1.35 ± 0.26	8.02 ± 2.33	11.48 ± 2.06	134.5 ± 2.7	140.3 ± 0.6
6 (+, -, +)	1.06 ± 0.11	1.41 ± 0.25	8.02 ± 0.92	8.54 ± 0.94	139.3 ± 1.5	142.3 ± 1.2
7 (+, +, -)	1.11 ± 0.35	1.34 ± 0.24	9.50 ± 1.08	8.96 ± 0.58	140.3 ± 2.5	139.0 ± 1.0
8 (+, +, +)	1.31 ± 0.16	1.10 ± 0.14	9.11 ± 0.30	8.50 ± 0.79	142.3 ± 1.5	142.3 ± 1.5

Table 4 showed that the amount of wood flour had a significant negative effect on the MFI of the original WPC, as was expected. Higher wood flour contents lowered the MFI and caused a high viscosity in the WPC. The rest of the relationships between the significant parameter(s) and measured responses will be elucidated with a similar approach. From the recorded unnotched impact strengths of the cured WPCs, it was concluded that the silane content showed a positive and significant effect, but the wood flour and talc contents had negative and significant effects. The addition of more silane would chemically initiate more crosslink bridges, especially in the cured samples. Hence, tight bonds with polymer chains would be formed. As a result, the WPC manufactured using a high silane loading would have a high impact strength. Excessive fiber and filler loadings in the WPC would reduce the toughness and impact strength of the material. Other significant effects and response property relationships will be described in a similar manner.

The determined regression equations were used to predict the properties of the WPCs manufactured according to the design formula in this research study. For example, with the regression model for HDT of the original WPC, the equation (138.52 + 2.81B + 1.81C) was resolved. A maximum HDT for the WPC was achieved when using a high level of wood flour (+B) and high level of talc (+C) in the twin screw extruder, and then the WPC was injected into test specimens at 190 °C. Other significant parameter(s) and properties were determined in an identical manner. By using the DOE approach, an initial formulation for manufacturing WPCs using macro crosslink PP can be determined and further refinement can then be conducted. Regarding to the DOE approach, after testing both the original and cured WPCs, the compounding formula of Run no. 7 (8 phr of silane, 35 phr of wood flour, and 20 phr of talc) was selected for further improvement.

Table 4. DOE Regression Models Used to Predict the WPC Properties

Test	Regression Models	
	Original	Cured
MFI	11.46 - 2.75(B)	-
Flexural strength	55.01 + 0.61(A) - 0.55(AC)	55.20 + 1.12(A) - 0.41(C) - 0.83(AC)
Flexural modulus	2.21 + 0.19 (C)	2.27 + 0.20(C)
Notched impact	Not significant	Not significant
Unnotched impact	Not significant	8.64 + 0.73(A) - 0.53(B) - 0.88(C)
HDT	138.52 + 2.81(B) + 1.81(C)	Not significant

Toughening of the WPCs Using UHMWPE

With the WPC formula selected from the DOE study (Run no. 7), the UHMWPE was considered for use as a toughener to further improve the toughness of the composite. The UHMWPE contents of 0 phr, 5 phr, 10 phr, 15 phr, 20 phr, and 25 phr, which corresponded to the PP, were studied. Consequently, six formulas were constructed, and they are shown in Table 5. The testing results obtained from both the original and cured injected samples are presented in Table 6.

Table 5. Formula for Toughening WPCs with UHMWPE

UHMWPE (phr)	PP (phr)	Silane (phr)	Wood (phr)	Talc (phr)	DCP (phr)	Stabilizer (phr)
0	100	8	35	20	0.3	2
5	100	8	35	20	0.3	2
10	100	8	35	20	0.3	2
15	100	8	35	20	0.3	2
20	100	8	35	20	0.3	2
25	100	8	35	20	0.3	2

As was expected, the MFI of the WPCs decreased, and there was a high viscosity as the UHMWPE content increased. It is well known that UHMWPE has a high molecular weight and is a long chain branching polymer. It has a high melting point and extreme melt viscosity. With the compounding temperature used in this work (190 °C), the high molar mass chain was not completely melted. Rather, it was probably softened and acted as a filler inside the WPC matrix. Consequently, by increasing the amount of UHMWPE, the flowability of the molten WPC was retarded, which was indicated by a drop in the MFI and increase in the shear viscosity.

The HDT of the WPC toughened with UHMWPE, within the marginal acceptable standard deviation, decreased for both the original and cured samples with increased UHMWPE content. After comparing the original and cured samples at a given UHMWPE content, an obvious increase in the HDT after sauna curing was noticed. The reduction in the HDT with increased UHMWPE content was explained by the fact that the HDT of the UHMWPE employed was 70 °C to 75 °C. This was much lower than the HDT of homo PP, which was approximately 110 °C. Using the rule of mixtures or Fox's equation, increasing the weight fraction of low HDT polymer (UHMWPE) to high HDT polymer results in a decreased HDT for the mixed polymers. There were two possible explanations for the increase in the HDT of the cured WPC. The macro crosslink between the peroxide

initiated silane grafted cellulosic wood fiber and PP chains was the primary suspect. The crosslinked WPC would have a higher HDT without the sauna treatment. Moreover, the crystallinity of a semi-crystalline polymer is typically increased after prolonged annealing at a temperature close to the HDT (Meekum 2014) and subsequently, an increase in the HDT of a few degrees is witnessed. In this study, the WPC was manufactured from semi-crystalline PP using a DCP/silane crosslink system, so it is reasonable to say that the increase in the HDT of the cured WPC samples was possibly driven by both explanations.

Table 6. Measured Properties of the WPCs Toughened by UHMWPE

UHMWPE (phr)	MFI (g/10min)	Impact Strength (kJ/m²)			
		Notched		Unnotched	
		Original	Cured	Original	Cured
0	4.961± 0.115	1.40 ± 0.60	1.49 ± 0.18	11.48 ± 1.28	12.77 ± 0.50
5	3.959 ± 0.039	1.88 ± 0.14	2.21 ± 0.33	12.55 ± 0.68	13.78 ± 0.86
10	3.601 ± 0.185	2.19 ± 0.11	2.24 ± 0.11	10.66 ± 1.10	11.10 ± 1.65
15	2.519 ± 0.059	2.03 ± 0.22	2.14 ± 0.14	11.13 ± 0.40	12.44 ± 0.81
20	2.391 ± 0.142	1.49 ± 0.01	2.01 ± 0.25	11.77 ± 0.82	12.07 ± 0.94
25	2.163 ± 0.067	1.31 ± 0.19	1.85 ± 0.14	11.82 ± 0.98	11.52 ± 1.25

UHMWPE (phr)	Flexural Properties				HDT (°C)	
	Strength (MPa)		Modulus (GPa)		Original	Cured
	Original	Cured	Original	Cured	135.0 ± 1.4	140.0 ± 1.0
0	57.10 ± 0.19	57.28 ± 1.12	2.35 ± 0.08	2.29 ± 0.13	138.3 ± 0.6	140.5 ± 2.1
5	53.99 ± 2.09	54.65 ± 0.56	2.09 ± 0.16	2.34 ± 0.07	134.7 ± 2.9	140.7 ± 2.1
10	51.95 ± 1.93	52.18 ± 0.91	2.07 ± 0.09	2.21 ± 0.11	130.3 ± 1.5	133.3 ± 0.6
15	50.62 ± 0.51	51.77 ± 0.86	1.88 ± 0.16	2.16 ± 0.11	128.0 ± 1.4	132.3 ± 1.2
20	49.14 ± 0.37	49.88 ± 1.57	1.93 ± 0.15	1.92 ± 019	128.5 ± 2.1	131.0 ± 1.0
25	48.48 ± 0.98	49.28 ± 0.80	1.84 ± 0.98	1.89 ± 0.15	135.0 ± 1.4	140.0 ± 1.0

For the Izod impact testing of the wood composites toughened by UHMWPE, the measured values are presented in Table 6. The notched impact strength of the WPCs showed an increasing trend as the UHMWPE increased from 0 phr to 10 phr. A decline in the strength was observed when the amount of UHMWPE was increased from 15 phr to 25 phr. The exact same phenomenon was found for both the original and cured samples. From the unnotched test results, it was quite difficult to determine the correlation between the strength and UHMWPE content. However, it was clearly seen that the unnotched impact strength of the WPC without UHMWPE was lower than that of the WPC with 5 phr of UHMWPE. The rest of the samples had a relatively constant impact strength. Another observation made was that the sauna treatment enhanced the impact strength. The improvement in the notched impact strength when the amount of UHMWPE increased from 0 phr to 10 phr could have been caused by the effectiveness of the compound as a toughener. Further increasing the UHMWPE loading caused an inferior impact strength, which could have been because of the agglomeration of UHMWPE particles. As was stated earlier, the WPC was processed at a low temperature and there was not enough heat to melt the UHMWPE. The formation of fiber-like macro crosslinks, resulting from the elongation of the softened UHMWPE particles under shear processing, was nevertheless expected. However, from the results of the SEM investigation given later in this section, no elongated chains were formed in this system. At a high UHMWPE content, it was observed that the particles only softened and then self-agglomerated into large lumps of UHMWPE, which accounted for the relationship between the mechanical properties and UHMWPE loading. The results indicated that the impact toughness of the WPCs became weak at high loadings.

Because of the superior impact toughness of the cured samples over that of the original samples, the silane/moisture induced crosslink/bonding reaction between the fiber and polymer needed to be clarified. From the impact strength results, it is highly recommended to use UHMWPE at a content below 15 phr for this WPC system.

In the case of the flexural properties, the strength and modulus of the WPC samples slowly decreased with an increasing UHMWPE loading for both the original and cured samples. Within the standard deviation of the error, it was observed that the flexural property values of the cured samples were marginally higher than those of the original samples. The inferior flexural properties as the UHMWPE content increased was because of the similar explanations given for the impact results. The main causes for the inferior flexural properties were the UHMWPE particle phase separation due to insufficient heat for melting and that no elongated macro fibers were formed to reinforce the material.

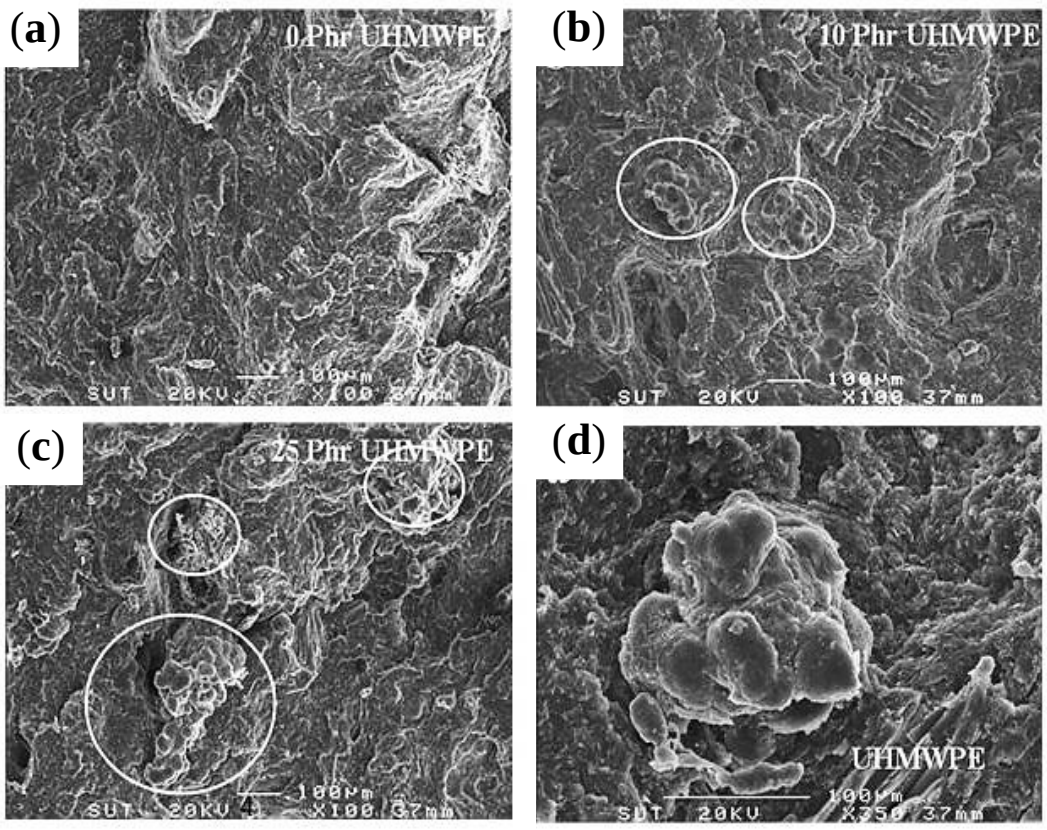

Fig. 3. SEM images of the original WPC samples with UHMWPE contents of (a) 0 phr, (b) 10 phr, (c) 25 phr (100× magnification), and (d) 10 phr (350× magnification)

The SEM photos of the surfaces of the notched impact specimens with UHMWPE contents of 0 phr, 10 phr, and 25 phr are given in Fig. 3. According to the SEM images, the interfacial adhesion bonding between the wood flour and PP matrix was reasonably good. There was no obvious separation between the fiber and matrix phases. There was no interfacial incompetency in this WPC system. A relatively poor dispersion of UHMWPE in the PP matrix phase was observed. The UHMWPE agglomerates, as indicated in the circles, grew bigger with an increasing UHMWPE content. Moreover, with the agglomeration of the UHMWPE particles and phase separation, poor adhesion with the PP matrix was clearly witnessed. This was reinforced by the SEM analysis at a higher magnification (300×), which is shown in Fig. 3d. Additionally, there was no SEM evidence

at any of the loadings of fiber-like macro elongated UHMWPE that would have been induced by the shearing during melt mixing or injection molding. The results of the SEM investigation supported the conclusions previously drawn about the relationship between the toughness properties (impact strengths and flexural properties) and UHMWPE loading. A high addition of UHMWPE to the WPC generally decreased the toughness properties mainly because of the agglomeration of UHMWPE particles.

From the above results of the mechanical properties testing, particularly for the impact strengths, two observations were made: (i) the marginal improvements to the properties were achieved by the sauna treatment and (ii) the impact strengths were superior with a loading of up to 10 phr of UHMWPE. Therefore, a careful SEM investigation on the WPC samples loaded with 10 phr of UHMWPE was conducted at a higher magnification. Figures 3b and 4a are the 500× magnification SEM photographs of the 10-phr UHMWPE-loaded WPCs before and after sauna curing, respectively.

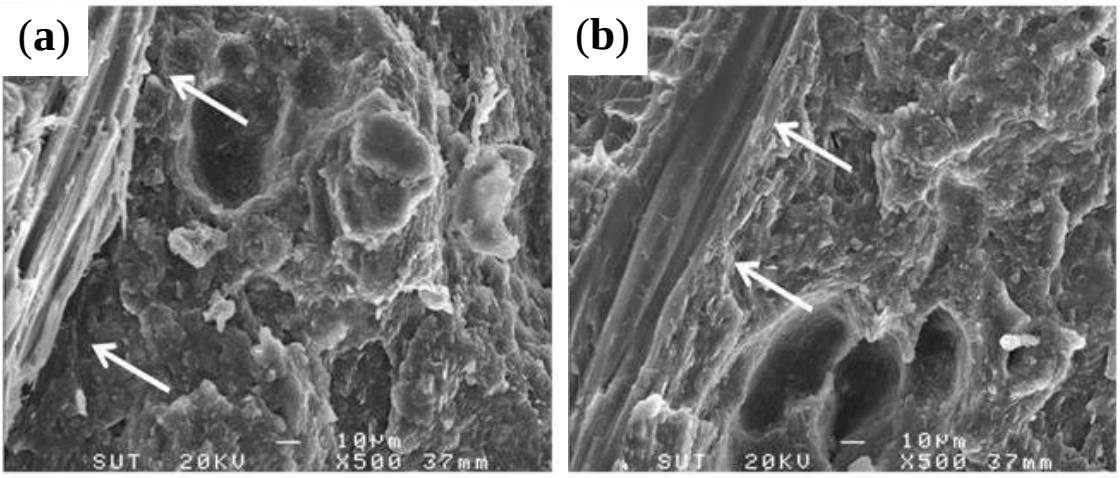

Fig. 4. SEM images at 500× magnification of the WPCs with 10 phr UHMWPE loading: (a) original and (b) cured

After comparing the original and cured samples, it was clearly seen that the interfacial adhesion between the wood flour fiber and PP matrix, indicated by the arrows in the SEM photographs, was improved by the sauna curing. The diminishing of the fiber and matrix gap after the sauna incubation was apparent. This observation supported the claim that interfacial adhesion bonding is effectively developed by the silane/moisture condensation reaction through prolonged sauna incubation. However, an increase in the crystallinity of the semi-crystalline PP matrix because of prolonged annealing at high temperature was not seen. This phenomenon also had a positive effect on the mechanical properties; however, it was not clearly revealed by the SEM investigation. With the marginal improvement to the properties by the sauna treatment, it was difficult to make a clear-cut judgement as to which phenomenon had a significant effect on this system. Without bias, the interfacial improvement by the silane/moisture treatment was preferred by this system. This was because, in polymer characteristics, a high crystallinity typically means a low fracture toughness. In the high magnification SEM photos, an improvement of the adhesion between the UHMWPE particles and PP matrix from the sauna curing was not seen. The debonding incident during fracturing under impact energy was clearly seen, as evidenced by the smooth surface holes on both the original and cured samples. The holes represented traces of the UHMWPE particles before their debonding under the fracturing

of the surface. With good adhesion, the UHMWPE can resist crack propagation. Hence, an outstanding notched impact strength would be recorded. In this work, such an observation was not found after either the sauna treatment or by increasing the UHMWPE loading.

From the above discussion, it was suggested that an improvement to the fracture toughness of the WPC material could be achieved by adding a small amount of UHMWPE (not exceeding 10 phr). However, the flexural properties and HDT were slightly insufficient at this level, assumingly because of the agglomeration of unmelted UHMWPE. The sauna curing was shown to be a decent treatment for the enhancement of the fiber and matrix interfacial adhesion. Hence, a marginal superiority in the fracture toughness was observed.

EPDM Toughening

Further improvement to the fracture toughness of the WPC was attempted. Using the WPC formula that contained 10 phr of UHMWPE, the effect of EPDM on the toughness was studied. Table 7 shows the rubber-toughened WPC formulas with EPDM contents that varied from 0 phr to 10 phr. The powdered ingredients, except for the wood flour, were plasticized with the rubber in the two-roll mill. Rubber compound flakes were obtained by deep freezing and crushing, as was described in the experimental section. With this process, feeding material into the twin screw extruder was easy. The WPC compound was then injection molded into the test specimens.

Table 7. WPC Formulas with EPDM as the Toughener

UHMWPE (phr)	EPDM (phr)	PP (phr)	Silane (phr)	Wood (phr)	Talc (phr)	DCP (phr)	Stabilizer (phr)
10	0	100	8	35	20	0.3	2
10	2	100	8	35	20	0.3	2
10	4	100	8	35	20	0.3	2
10	6	100	8	35	20	0.3	2
10	8	100	8	35	20	0.3	2
10	10	100	8	35	20	0.3	2

Table 8 summarizes the test results of the WPC toughened with EPDM rubber. The MFI gradually decreased with a high viscosity and increased EPDM content. Two explanations for this were determined. First, rubber normally has a high viscosity, and a higher rubber content results in a higher compound viscosity. Secondly, in the presence of DCP, which was adopted in this system, rubber crosslinking is induced by the free radical initiator during high temperature compounding processes. Consequently, the viscosity of the WPC should increase with an increased rubber loading. For the system studied, rubber crosslinking most likely occurred, which resulted in the low MFI and increased viscosity.

The relationship between the HDT and amount of EPDM, which is summarized in Table 8, indicated that there was a declining trend with the rubber loading for both the original and cured samples. Upon closer observation, the degree to which the HDT decreased with increasing EPDM was found to be smaller for the cured WPCs than for the original WPCs. Moreover, at a given EPDM content, the service temperature (HDT) of the WPC was increased by the sauna treatment. The HDT decreased with increased EPDM content, which was expected. In fact, according to the rule of mixtures, mixing very low HDT EPDM rubber into the PP-based WPC must have an effect on the HDT of the final WPC. By conducting a sauna treatment on the sample, two crosslink sites, *via* silane/moisture condensation, likely occurred between the silane grafted wood fiber and

PP chain and silane grafted fiber and EPDM network chains (Meekum and Kingchang 2017). During thermosetting, the crosslinking of the polymer, characteristics of the WPC, and HDT of the composite wood sample increased. Additionally, with the fiber/crosslink EPDM rubber bridge, the HDT of the sauna cured WPC did not decrease much with an increased rubber loading. With regards to the obtained results, the HDT of the cured WPC was approximately 133 °C for all of the formulas. Another factor that had a positive effect on the HDT of the cured WPC samples was the increase in the crystallinity of the semi-crystalline PP matrix. As was mentioned earlier, prolonged annealing of the PP at a temperature close to or slightly above its glass transition temperature can cause an increase in the crystallinity of the polymer chains. Consequently, the HDT increased after 12 h of sauna incubation at 105 °C.

Table 8. Effect of the EPDM Toughener on the WPC Properties

EPDM (phr)	MFI (g/10min)	Impact Strength (kJ/m^2)			
		Notched		Unnotched	
		Original	Cured	Original	Cured
0	3.303 ± 0.123	1.80 ± 0.27	2.41 ± 0.15	11.62 ± 0.17	11.82 ± 1.37
2	2.905 ± 0.036	2.20 ± 0.11	2.62 ± 0.14	11.83 ± 1.16	11.92 ± 0.61
4	2.633 ± 0.041	2.82 ± 0.11	3.23 ± 0.22	12.05 ± 0.77	12.57 ± 1.06
6	2.698 ± 0.034	2.97 ± 0.21	3.60 ± 0.14	12.58 ± 0.99	12.74 ± 0.56
8	2.433 ± 0.133	3.22 ± 0.21	3.87 ± 0.29	12.44 ± 1.15	12.45 ± 0.92
10	2.429 ± 0.091	3.68 ± 0.15	4.23 ± 0.19	12.72 ± 1.67	12.66 ± 1.13

EPDM (phr)	Flexural Properties				HDT (°C)	
	Strength (MPa)		Modulus (GPa)		Original	Cured
	Original	Cured	Original	Cured	133.7 ± 0.6	135.3 ± 1.2
0	48.50 ± 0.82	49.19 ± 1.55	1.81 ± 0.17	2.00 ± 0.08	123.0 ± 0.0	133.7 ± 1.5
2	44.01 ± 0.56	46.32 ± 0.35	1.81 ± 1.16	1.85 ± 0.15	123.3 ± 2.0	132.7 ± 0.6
4	42.41 ± 0.92	42.67 ± 0.92	1.70 ± 0.77	1.74 ± 1.04	121.3 ± 0.6	132.0 ± 1.0
6	40.19 ± 0.55	39.87 ± 0.69	1.57 ± 0.99	1.62 ± 0.01	119.3 ± 0.6	132.3 ± 0.6
8	37.63 ± 0.68	38.83 ± 0.71	1.54 ± 1.15	1.52 ± 0.65	119.0 ± 0.0	132.7 ± 0.6
10	37.96 ± 0.50	38.19 ± 0.90	1.51 ± 0.03	1.51 ± 0.01	133.7 ± 0.6	135.3 ± 1.2

The test results of the impact strengths (notched and unnotched) conducted on both the original and cured WPCs are illustrated in Table 8. As was expected, the impact strengths, especially the notched one, displayed an obviously increasing trend with the EPDM loading. A high degree of improvement was found for the notched impact strength. Meanwhile, a gradual increase was observed for the unnotched strength. It was also seen that the sauna treatment undoubtedly enhanced the impact strengths, especially the notched strength. The maximum strengths were found for the sample produced with 10 phr of EPDM. As was previously discussed, adding more rubber to the WPC would enhance the impact energy absorption/dissipation during rapid crack propagation, especially at the V-notched tip stress concentration. Hence, the fracture toughness of the rubber-toughened WPCs was enhanced. As was also stated above, crosslinking between the silane grafted wood fiber/PP chain and silane grafted fiber/EPDM occurred. These chemically bonded fibers had a positive effect on the interfacial adhesion between those phases. Consequently, a further increase in the crack propagation resistance resulted from the sauna incubation process. The impact strengths of the cured WPCs were superior to those of the original WPCs. These results were in good agreement with the WPC system using HDPE/PP blend as the matrix using 10% EPDM as toughener (Clemons 2010)

At the very low rate of crack propagation applied during the flexural bending testing, the flexural strengths and moduli of both the original and cured samples slowly decreased with an increasing EPDM content. Meanwhile, at a given amount of rubber, the silane/moisture treatment marginally increased the flexural properties. The decrease in both the flexural strength and modulus at higher EPDM contents was explained by the rubbery characteristics of the WPC material. This meant that a more ductile material was obtained. This was emphasized at higher rubber loadings, where the WPCs became more rubbery. This statement was in good agreement with the HDT results. With the crosslinking, *via* sauna incubation, the thermosetting characteristic overcame the ductility of the WPC. Then, the ductility was diminished and the WPC became brittle. As a result, a lower flexural strength and higher modulus were observed. The crystalline formation of the PP matrix, because of prolonged annealing at a high temperature, likely contributed to the material brittleness as well.

The SEM images of the notched fractured surface of the WPC samples with 0 phr and 10 phr of EPDM are presented in Fig. 5. Figures 5a and 5b show the original and cured samples, respectively, and there was a visible gap, indicated by the arrows, between the wood fiber/matrix in the original sample.

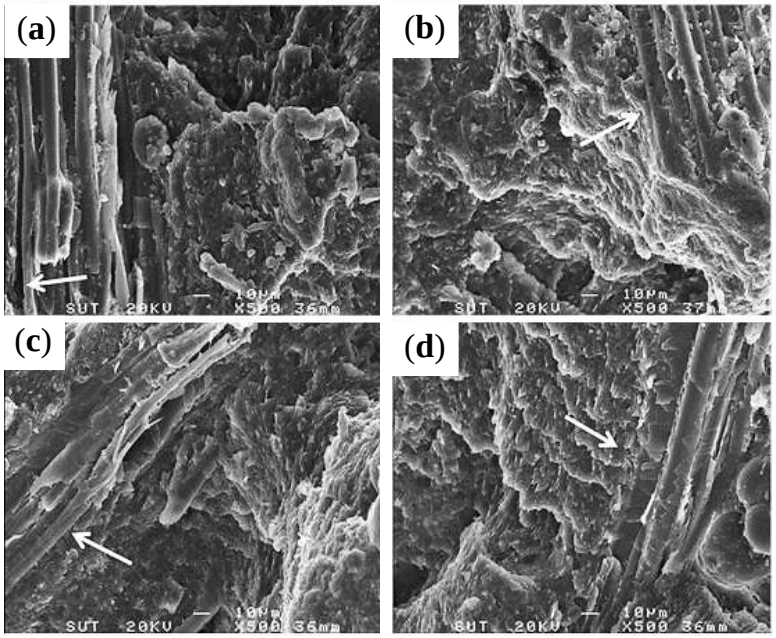

Fig. 5. SEM photos at 500× magnification of the fracture surfaces of the WPC with EPDM contents of (a) 0 phr (original), (b) 0 phr (cured), (c) 10 phr (original), and (d) 10 phr (cured)

After the sauna treatment, excellent contact between those phases was observed. This piece of evidence confirmed the presence of a network formation between the silane grafted wood flour and PP matrix caused by the silane/moisture condensation reaction. As a result, the impact and flexural properties of the sauna cured WPCs were superior to those of the original samples. After comparing the SEM photos of the original and cured WPCs with 10 phr of EPDM, which are presented in Figs. 5c and 5d, respectively, not only was a better fiber/matrix adhesion seen, but also rougher fractured traces of the matrix were noticed on the cured sample. This was the outcome of crosslinking between the PP chain and peroxide-initiated EPDM network *via* the silane/moisture condensation reaction. A rougher sample surface indicated a higher impact toughness. These SEM results were in

agreement with the notched impact testing results, where an improvement to the impact strength was found after prolonged sauna incubation.

After adopting a higher SEM magnification (750×), the interfacial adhesion between the UHMWPE and PP matrix blended with 0 phr and 10 phr EPDM was investigated for the original samples. The obtained SEM photos are shown in Fig. 6. For the rubber-toughened WPC, fibril-like structures, indicated by the arrows, were clearly observed in the UHMWPE/PP matrix adhesion interface. Meanwhile, no such phenomenon was apparent in the sample without EPDM. This indicated that the adhesion between the PP, unmelted UHMWPE, and EPDM must have resisted crack propagation during the impact testing. Hence, the impact strength of the WPC must have been improved by adding EPDM into the silane/peroxide crosslink PP matrix system. This SEM finding was reinforced by the previous conclusion that higher EPDM loadings resulted in higher impact strengths.

According to the SEM investigation, the sauna treatment improved the fiber/matrix adhesion. Thus, the sauna cured sample had a better impact strength than the original sample. Moreover, the impact strength increased with an increasing EPDM rubber content, which was determined by the following positive effects: (i) the matrix toughness was improved and (ii) there was better UHMWPE/PP interfacial adhesion at high rubber contents. These phenomena arose from the silane/moisture condensation reaction.

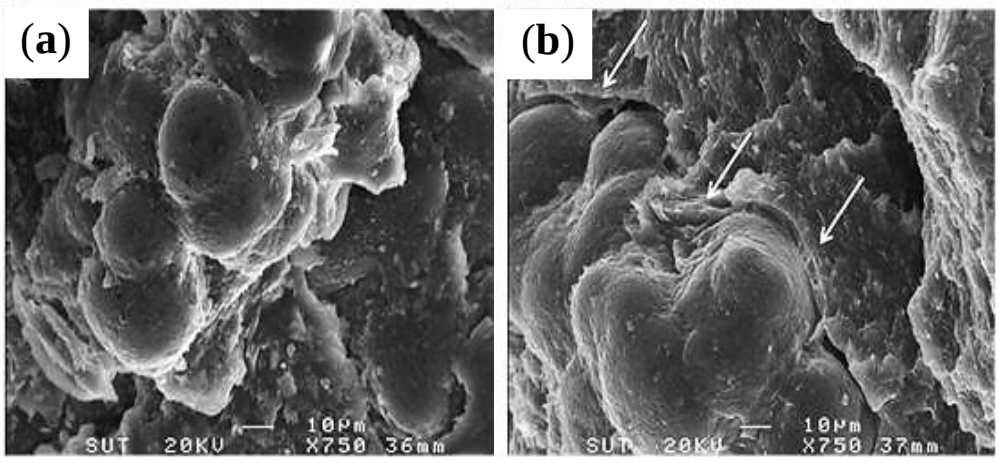

Fig. 6. SEM photos at 750× magnification of the original WPC with (a) 0 phr and (b) 10 phr of EPDM

CONCLUSIONS

1. A 2^3 DOE approach was used to investigate the preliminary formula for manufacturing WPCs. The statistical conclusion suggested that WPC compounding formula with 8 phr of silane, 35 phr of wood flour, and 20 phr of talc was initially established to improve the toughness property.
2. When attempting to use UHMWPE as a fracture toughener for the WPC based on a silane/peroxide macro crosslink PP system, a loading of up to 10 phr of UHMWPE was found effective. The flexural properties and HDT were slightly insufficient at the optimum UHMWPE content (10 phr). Exceeding the optimum loading level resulted in the agglomeration of unmelted UHMWPE particles. Hence, the mechanical

properties were inferior at high UHMWPE contents. Enhancement of the fiber and matrix interface was successful with the sauna treatment. Consequently, a marginal increase in the fracture toughness was observed.

3. The impact strengths were increased by adding EPDM as a rubber toughener to the silane/peroxide macro crosslink PP matrix system. However, higher EPDM concentrations resulted in lower HDT values. The sauna treatment of the EPDM-toughened WPC enhanced the impact strengths. The better fiber/matrix adhesion caused by the silane/moisture condensation was explained. The effectiveness of adding EPDM as a rubber toughener in WPCs was determined by the following two positive effects: (i) the PP matrix toughness was improved and (ii) there was better UHMWPE/PP interfacial adhesion.

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